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Elucidating Traffic Junction Effects in MFI Zeolite Using Kinetic Monte Carlo Simulations

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Supporting Information

ABSTRACT: Published experimental studies on the diffusion of n-butane (nC4)/iso-butane (iC4), n-hexane (nC6)/2-methylpentane (2MP), and methane/benzene mixtures in MFI zeolite show that the self-diffusivity of the more mobile (linear) alkanes is diminished by about 1–3 orders of magnitude with increasing proportion of the tardier partners (iC4, 2MP, benzene) in the mixture. The strong reduction can be rationalized on the basis of the preferential location of the tardier partners in the MFI topology, serving to slow down the molecular traffic. The primary objective of this article is to investigate, and quantify, such traffic junction effects with the aid of kinetic Monte Carlo (KMC) simulations. The KMC simulations show that the preferential location of branched molecules at the channel intersections can be effectively considered as an intersection blocking with attendant loss of connectivity of the MFI topology. Consequently, both the Maxwell–Stefan (M–S) diffusivity and self-diffusivity for nC4 in the nC4/iC4 mixtures are lowered below that for the unary nC4 diffusion by about 2 orders of magnitude.

It is also established that such a lowering of the diffusivity of the more mobile partner is distinctly different from the “correlation” effects that generally manifest in the mixture diffusion in microporous materials.

1. INTRODUCTION

MFI (= Mobil Five) zeolite, also called ZSM-5,1 is used as a catalyst or adsorbent in a wide variety of industrially important processes such as catalytic cracking, xylene isomerization, alkylation of benzene, and separation of alkane isomers.2−10 Thin perm-selective layers of MFI zeolite membrane separations for CO2 capture.11

MFI has a topology consisting of a set of intersecting straight channels and zigzag (or sinusoidal) channels (see Figure 1a). The channel dimensions are size of 5.5 Å.

A key feature of the mixture diffusion in MFI is that the mobility of any guest constituent is retarded due to the correlated molecular "jumps" (see Figure 1b). The exchange coefficient, δ12, that characterizes binary mixture diffusion, D1 and D2, and the degrees of correlations imply that the first right-hand members of eq 1 offer significant contributions to the intracrystalline fluxes, causing significant slowing-down effects.15,16 For H2(1)/CO2(2) permeation across the MFI membrane, for example, experimental data17 are well described by taking D1/D12 = 20.15,19 In this case, the more strongly adsorbed but tardier CO2 retards the mobility of the faster-diffusing but poorly adsorbed H2. In eq 1, R is the gas constant, ρ is the framework density, $\Theta_i$ are the component loadings expressed in molecules uc−1 (uc = unit cell), and xi are the component mole fractions defined as

$$x_i = \Theta_i/(\Theta_1 + \Theta_2); \ i = 1, 2 \tag{2}$$

The Onsager reciprocal relations impose the symmetry constraint

$$D_{12} = D_{21} \tag{3}$$

The M–S formulation (eq 1) is phenomenological and serves to define the three diffusivities $D_{11}$, $D_{22}$, and $D_{12}$ that characterize binary mixture diffusion. $D_{11}$ and $D_{22}$ characterize the species-wall interactions. The exchange coefficient $D_{12}$ quantifies the correlation effects that cause the slowing down of more mobile guest molecules. The degrees of correlations in the molecular jumps within the microporous channels are quantified by the ratios $D_{11}/D_{12}$ and $D_{22}/D_{12}$. High values of the degrees of correlations imply that the first right-hand members of eq 1.

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Molecular dynamics (MD) simulations of several binary mixtures in MFI zeolite, and other microporous materials, have established the M–S diffusivities \( D_{ij} \) and \( D_{ij} \) can be identified with the corresponding diffusivities for unary systems provided the values are determined at the same pore occupancy \( \theta \). The MD simulations also allow quantification of the degrees of correlations, \( D_i/D_{ij} \) and \( D_j/D_{ij} \).

A special scenario emerges for the mixtures containing branched alkanes and aromatics. Figure 1b presents the PFG NMR data on the self-diffusivities of \( n \)-butane \( (nC4) \) in the binary mixtures of \( n \)-butane \( (nC4) \) with iso-butane \( (iC4) \) in which the total loading, \( \Theta_i = \Theta_{nC4} + \Theta_{iC4} \), is held constant at 4 molecules uc\(^{-1}\). Increase in the loading of the \( iC4 \) from \( \Theta_{iC4} = 0 \) to 2 molecules uc\(^{-1}\) has the effect of reducing the self-diffusivity of \( nC4 \) by about 2 orders of magnitude. As evidenced in the computational snapshot in Figure 1a, the tardier constituent \( iC4 \) prefers to locate at the channel intersections. The diffusivity of \( iC4 \) is lower than that of \( nC4 \) by 3 orders of magnitude. The occupation of some of the intersection sites by \( iC4 \) may be viewed as effective blockage of the molecular traffic within the channels.

Figure 1c shows the experimental data on the self-diffusivities in the binary mixtures of \( n \)-hexane \( (nC6) \) with 2-methylpentane \( (2MP) \) in MFI in which the total loading is \( \Theta_i = \Theta_{nC6} + \Theta_{2MP} = 3.8 \) molecules uc\(^{-1}\). The preferential location of the tardier \( 2MP \) at the channel intersections causes a reduction in the self-diffusivity of \( nC6 \) by about an order of magnitude.

With increase in the loading of benzene \( (Bz) \), the self-diffusivity of \( CH_4 \) in binary \( CH_4/Bz \) mixtures is reduced by about 2 orders of magnitude (see Figure 1d). The explanation is again to be found in the reduction of \( CH_4 \) diffusivity due to the blockage of the intersections by benzene. In the process of the alkylation of benzene using H-ZSM-5 catalyst to produce ethylbenzene, the tardier aromatic molecules prefer to locate at the channel intersections. The blocking of the intersections by the aromatic guests causes a severe reduction in the effective diffusivity of the reactant \( C_2H_4 \).

The primary objective of this article is to examine the characteristics of the M–S diffusivities \( D_{ij} \), \( D_{ij} \), and \( D_{ij} \) applicable to the traffic junction phenomena witnessed in Figure 1. Specifically, we aim to show that for diffusion in the \( nC4(1)/iC4(2) \) mixtures, the M–S diffusivity of the more mobile \( nC4 \), \( D_{ij} \), is significantly lower than that of the corresponding unary \( nC4 \). Furthermore, we shall establish that the reduction in the diffusivity of \( nC4 \) is not attributable to the usual “correlation” effects. Due to the extremely low values of the diffusivities of \( iC4 \), the MD simulations of the \( nC4/iC4 \) diffusion to determine the M–S diffusivities are of low accuracy and also computationally expensive. For this reason, we resort to the kinetic Monte Carlo (KMC) simulations using the methodology detailed in earlier publications.

2. COMPUTATIONAL METHODS: KMC SIMULATIONS
The KMC simulation methodology employed for the MFI lattice topology is shown schematically in Figure 2. Per unit cell, highlighted in orange in the inset, is made up of 12 adsorption sites.
and zigzag channels when moving toward the intersections. Based on the MD simulations of the self-diffusivities of guest molecules in \( x, y, z \)-directions (see Figure S13),\(^{32} \) it is concluded that the frequency along the straight channels \( \nu_{\text{str}} \) is greater than that along the zigzag channels \( \nu_{\text{zz}} \) by a factor of about 2. Further details of the KMC simulation methodology are provided in the Supporting Information.

### 3. RESULTS AND DISCUSSION

We first undertake the KMC simulations of the \( n\text{C}4/i\text{C}4 \) mixture diffusion to match with the experiments of Fernandez et al.\(^{21} \) in Figure 1b. The preferential location of branched alkanes, such as \( i\text{C}4 \), at the intersection sites can be modeled by taking the jump frequencies away from the intersection sites to be lower by a factor \( f \) than the corresponding frequencies \( \nu_{\text{str}} \) and \( \nu_{\text{zz}} \).\(^{31} \) This factor \( f \) is determined by the ratio of the Langmuir constants in the dual-site Langmuir fits

\[
q = \frac{b_{\text{pp}}}{1 + b_{\text{pp}}} + \frac{b_{\text{ip}}}{1 + b_{\text{ip}}} \tag{4}
\]

for the unary \( i\text{C}4 \) isotherm at 363 K in Figure 3a; we determine \( f = b_{\text{ip}}/b_{\text{pp}} = 0.001 \); calculation details are provided in the Supporting Information. For \( n\text{C}4 \), there are no perceptible isotherm inflections, and the jump frequencies toward and away from the intersection sites are equal, i.e., \( f = 1 \). With the chosen values of the jump frequencies \( \nu_{\text{str}} \) and \( \nu_{\text{zz}} \) for \( n\text{C}4 \) (\( \nu_{\text{str}} = 4 \times 10^9 \text{ s}^{-1}; \nu_{\text{zz}} = 2 \times 10^9 \text{ s}^{-1}; f = 1 \)) and \( i\text{C}4 \) (\( \nu_{\text{str}} = 4 \times 10^9 \text{ s}^{-1}; \nu_{\text{zz}} = 2 \times 10^9 \text{ s}^{-1}; f = 0.001 \)), the KMC simulations of the self-diffusivities are shown in Figure 3b; the reduction in the \( n\text{C}4 \) self-diffusivity by 2 orders of magnitude with increasing \( i\text{C}4 \) loadings are in line with the experimental data in Figure 1b.

Remarkably, the M–S diffusivity \( D_i \) for \( n\text{C}4 \) also shows a lowering of 2 orders of magnitude with increasing proportions of \( i\text{C}4 \) in the mixture (see Figure 3c). Within the framework of the M–S formulation (eq 1), a reduction in \( D_i \) does not fall within the purview of the “correlation effects”. For the transient uptake of the \( n\text{C}6/2\text{MP} \) mixtures in MFI zeolite crystals, Titze et al.\(^{33} \) found that the M–S diffusivities of both \( n\text{C}6 \) and 2MP decrease strongly with increasing 2MP loading, which is analogous to that observed Figure 3c. Indeed, for \( n\text{C}6/2\text{MP} \) separations in fixed beds of MFI zeolite, both intracrystalline diffusion and mixture adsorption in the MFI favor the linear isomer, leading to the highly effective separations in fixed-bed adsorption devices.\(^{18,33,34} \)

Figure 4a shows KMC simulations for \( n\text{C}4/2\text{MP} \) mixtures in which the chosen jump frequencies of the bulkier 2MP are taken to be a factor 10 lower than those for \( i\text{C}4 \): \( (\nu_{\text{str}} = 4 \times 10^9 \text{ s}^{-1}; \nu_{\text{zz}} = 2 \times 10^8 \text{ s}^{-1}; f = 0.001) \). The reduction of the M–S diffusivity of \( n\text{C}4 \) is practical the same as that for \( i\text{C}4 \), even though 2MP is 10 times tardier than \( i\text{C}4 \); this finding strengthens the hypothesis that the lowering is not caused by correlated hops in the MFI channels. The KMC simulations for the mixtures of propane(C3)/\( i\text{C}4 \) mixtures, wherein the jump frequencies of C3 are a factor of 2 higher than those for \( n\text{C}4 \), show that the influence of increased \( i\text{C}4 \) loading on the M–S diffusivities of the linear alkanes are entirely analogous (see Figure 4b).

To demonstrate that the results in Figures 3 and 4 are distinctly different from the correlation effects, we performed KMC simulations for \( n\text{C}4 \) in partnership with a “hypothetical” guest species \( i\text{C}4^* \) in which the jump frequencies for \( i\text{C}4^* \) are prescribed as \( (\nu_{\text{str}} = 4 \times 10^7 \text{ s}^{-1}; \nu_{\text{zz}} = 2 \times 10^7 \text{ s}^{-1}; f = 1) \), i.e., a factor of 10\(^3 \) lower than those for \( n\text{C}4 \) but without preference to locate at the intersections. Figure 5a compares the M–S diffusivities for the \( n\text{C}4/i\text{C}4 \) and \( n\text{C}4/i\text{C}4^* \) mixture diffusion; these show that the M–S diffusivities for the hypothetical
nC4/iC4* mixture are independent of iC4* loading, as expected for “normal” mixtures without preferential locations of guest molecules. The corresponding values of the self-diffusivities are compared in Figure 5b. The self-diffusivity of nC4 in the nC4/iC4 mixtures is reduced by a factor of about 3, whereas the corresponding reduction for the nC4/iC4* mixtures is reduced by 2 orders of magnitude. The inescapable conclusion to be drawn from the KMC simulations in Figure 5 is that traffic junction effects do not fall under the category of correlation effects.

To unravel the reasons for the reduction in the M–S diffusivity of nC4, with increased iC4 loading, we undertook KMC simulations in which certain number of intersection sites in the 2 × 2 × 4 = 16 unit cells are selected and subsequently deleted, along with the connections to the adjoining straight and zigzag channels. The blocking and deletion procedure is illustrated in Figure 6; further elaboration and details are available in the Supporting Information. Evidently, blocking of the intersection sites results in a decrease in the connectivity of the MFI topology. Five different % blocking effects were simulated: 6.25, 12.5, 25, 37.5, and 50%, corresponding to the deletion of 4, 8, 12, 18, and 32 of the total 64 intersection sites in the 2 × 2 × 4 simulation box.

Figure 4. (a) KMC simulation results for M−S diffusivities of nC4 in the nC4/iC4 and nC4/2MP mixtures (total loading is held constant at 4 molecules uc⁻¹) as a function of the loading of the branched alkane. (b) KMC simulation results for the M−S diffusivities of linear alkanes in the C3/iC4 and nC4/iC4 mixtures (total loading is held constant at 4 molecules uc⁻¹) as a function of the loading of the branched alkane. Further computational details are provided in the Supporting Information.

Figure 5. KMC simulation results for (a) M−S diffusivities and (b) self-diffusivities for (a) nC4/iC4 and nC4/iC4* mixture diffusion (total loading is held constant at 4 molecules uc⁻¹) as a function of iC4 or iC4* loading. Further computational details are provided in the Supporting Information.

Figure 6. MFI topology in which the intersection site at the center is blocked and the adjoining connections are deleted (indicated by crosses).

Figure 7 presents the KMC simulation results for the influence of the degree of intersection blocking on the M−S diffusivity, D₁, and degrees of correlation, D₁/D₁', for the nC4 diffusion in the MFI zeolite. The unary M−S diffusivities are well described by
where $D_{1(0)}$ is the M–S diffusivity at “zero-loading”, and the fractional occupancy $\theta$ is the total loading divided by the total number of available adsorption sites after the deletion of the selected number of intersection sites. For the unblocked topology, the zero-loading M–S diffusivity is $D_{1(0)} = 3.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The zero-loading M–S diffusivity $D_{1(0)}$ decreases exponentially with the number of blocked intersection sites in one unit cell, $3.7 \times 10^{-9} \exp(-1.0 \Theta_{\text{blocked}})$ (see Figure 7b).

The dashed lines in Figure 4a,b compare the exponential decay model with the KMC data for the nC4/iC4, nC4/2MP, and C3/iC4 mixtures. Though there are some quantitative differences, the exponential decay model captures the essential characteristics of the reduction in the M–S diffusivity of linear alkanes, suggesting that traffic junction effects are primarily attributable to significant decrease in the connectivity of the MFI topology by blocked intersections.

4. CONCLUSIONS

Kinetic Monte Carlo simulations, in conjunction with the Maxwell–Stefan diffusion formulation, were used to investigate the traffic junction effects that manifest for the mixtures of linear alkane and branched alkanes. The KMC simulations of the nC4/iC4, nC4/2MP, and C3/iC4 mixtures at a constant total loading of 4 molecules per unit cell serve to establish that the diffusivity of the linear alkane suffers a decrease of about 2 orders of magnitude when the loading of the branched partner molecule is increased; this is in line with the published experimental data. The reasons for this reduction in the diffusivity of the linear alkane are unequivocally traceable to the loss of connectivity in the MFI topology due to the effective blocking of the intersection sites by ensconced branched molecules. The KMC simulations also establish that traffic junction effects are distinctly different from the correlation effects that manifest for the mixtures in which none of the components exhibits preferential adsorption at the intersection sites.

The results of this study have ramifications for the implementation of the Maxwell–Stefan diffusion model in the design of catalytic reactors, fixed-bed adsorbers, and membrane permeation devices.8,9,18

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01369.

Provides (a) the structural details for MFI zeolite, (b) Maxwell–Stefan diffusion formulation, (c) kinetic Monte Carlo simulation methodology, including procedures for the calculation of the Maxwell–Stefan diffusivities, (d) KMC simulation data for unary and binary systems (PDF).

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Notes

The authors declare no competing financial interest.

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Latin Alphabet

D, Maxwell–Stefan diffusivity for molecule–wall interaction, m² s⁻¹
D(0), M–S diffusivity at zero loading, m² s⁻¹
Dₑ₂, M–S exchange coefficient for binary mixture, m² s⁻¹
Dₑ₂, self-diffusivity of species i, m² s⁻¹
fₛ, ratio of frequencies away and toward intersections, dimensionless
Nᵢ, molecular flux of species i with respect to framework, molecules m⁻² s⁻¹
R, gas constant, 8.314 J mol⁻¹ K⁻¹
T, absolute temperature, K
xᵢₒ, mole fraction of species i in adsorbed phase, dimensionless

Greek Alphabet

µᵢ, molar chemical potential of component i, J mol⁻¹
θᵢ, fractional occupancy, dimensionless
Θᵢ, loading of species i, molecules uc⁻¹
νᵢ, jump frequency, s⁻¹
ρᵢ, framework density, uc m⁻³

Subscripts

1, referring to component 1
2, referring to component 2

■ REFERENCES